OPTICAL ABSORPTION SPECTRA OF SILVER ATOMS STABILIZED IN VARIOUS MATRICES AT 77°K

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Abstract

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OPTICAL ABSORPTION SPECTRA OF SILVER ATOMS STABILIZED IN VARIOUS MATRICES AT 77°K

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In work (^{1}), by means of x-ray irradiation at 77°K of frozen solutions of silver salts, free silver atoms stabilized in such media were obtained. In the same work, the properties of these stabilized atoms in the ground state were studied by the method of paramagnetic resonance. The present communication contains information on the first results of a study of the optical properties of such stabilized silver atoms, which also makes it possible to begin studying the behavior of these atoms in excited states.

Below we present the optical absorption spectra obtained by us for silver atoms stabilized in aqueous and alcoholic solutions of its salts irradiated at 77°K. In this case the alcoholic solutions were frozen by immersing a quartz test tube containing the solution directly into liquid nitrogen, and the samples studied probably had the structure of amorphous ice. The aqueous solutions, on the other hand, were first slowly frozen in the freezer compartment of a household refrigerator, after which samples were broken out of them and then lowered into liquid nitrogen. These samples were apparently single crystals. Usually, after irradiation, they underwent brief low-temperature annealing, which led to splitting and a sharp narrowing of the spectral lines. Here results will be given only for such annealed samples.

The absorption spectra of silver atoms formed in such frozen solutions after their x-ray irradiation at 77°K are shown in Fig. 1. These spectra were also recorded at 77°K. In the upper part of the figure the arc emission spectrum of silver is presented. Two lines are visible, associated with the transitions $^2S_{1/2} \rightarrow {}^2P_{1/2}$ and $^2S_{1/2} \rightarrow {}^2P_{3/2}$ in free neutral silver atoms. Transitions between the ground term ^2S and the first excited term ^2P must also be present and be the most intense in the absorption spectra of silver atoms. Below in Fig. 1 are given the absorption spectra of silver atoms stabilized in various frozen aqueous and alcoholic solutions. The similarity of these absorption spectra for different matrices is evident, but differences are also noticeable, caused by the different nature of these matrices. The figure presents results for solutions of

Figure 1

Figure 1: Figure 1

the salt AgF. Spectra analogous to those shown in the figure were obtained with solutions of the salt $AgNO_3$ in ethyl and propyl alcohols. The arc spectrum of iron was used for calibrating the absorption spectra.

Before recording the optical absorption spectra, the content of stabilized silver atoms in the samples was studied by the method of paramagnetic resonance ([1]). Numerous special control experiments were also carried out, confirming that the absorption lines under consideration in Fig. 1 owe their origin to stabilized silver atoms.

Table 1 gives the wavelengths for the maxima of the absorption lines of stabilized silver atoms, as well as the half-widths of these lines.

Fig. 1. Absorption spectra of silver atoms stabilized in frozen aqueous and alcoholic solutions of its salts, irradiated at 77°K. Capital letters denote spectral lines for aqueous solutions, lowercase letters those for alcoholic solutions.
1 –Ag, arc; 2 –$H_2O + AgF$; 3 –$H_2O + AgF$; 4 –$D_2O + AgF$; 5 –$CH_3OH + AgF$; 6 –$C_4H_9OH + AgF$; 7 –$C_3H_7OH + AgF$; 8 –$C_2H_5OH + AgF$; 9 –Fe, arc.

The absorption spectra under consideration of stabilized silver atoms can apparently be regarded as consisting of doublets (possibly A and B, E and Zh in aqueous solutions, and a and b, e and zh in alcoholic ones) and triplets (V, G, D and, possibly, the unresolved triplet v, g, d). A doublet or triplet in these spectra may appear as a result of the lifting, by the electric field of the matrix, of the degeneracy with respect to the quantum number of the orbital mo—

Table 1

	Matrix	Wavelength of line maxima, Å	Line width, cm^{-1}	Matrix	Wavelength of line maxima, Å	Line width, cm^{-1}
	Free atom	3383				
	Free atom	3281				
A	$H_2O + AgF$	3723 ± 30	940	$D_2O + AgF$	3700 ± 30	1100
B	$H_2O + AgF$	3380 ± 15	1660	$D_2O + AgF$	3365 ± 15	1320
V	$H_2O + AgF$	3195 ± 10	740	$D_2O + AgF$	3156 ± 30	1300
G	$H_2O + AgF$	3100 ± 10	830	$D_2O + AgF$		

	Matrix	Wavelength of line maxima, Å	Line width, cm^{-1}	Matrix	Wavelength of line maxima, Å	Line width, cm^{-1}
D	H_2O + AgF	3020 ± 10	880	D_2O + AgF	3053 ± 15	860
E	H_2O + AgF	2860 ± 15	980	D_2O + AgF	2900 ± 25	950
Zh	H_2O + AgF	2645 ± 20(?)		D_2O + AgF		
a	C_2H_5OH + AgF	3673 ± 30	1700	C_3H_7OH + AgF	3680 ± 30	1860
b	C_2H_5OH + AgF	3267 ± 10	470	C_3H_7OH + AgF	3270 ± 10	510
v, g, d	C_2H_5OH + AgF	3030 ± 20	2180	C_3H_7OH + AgF	3070 ± 20	1490
e	C_2H_5OH + AgF	2850 ± 15	620	C_3H_7OH + AgF		
zh	C_2H_5OH + AgF	2757 ± 15(?)		C_3H_7OH + AgF		
a	C_2H_5OH + $AgNO_3$	3660 ± 30	1940	C_3H_7OH + $AgNO_3$	3670 ± 40	1780
b	C_2H_5OH + $AgNO_3$	3270 ± 10	470	C_3H_7OH + $AgNO_3$	3270 ± 10	470
v, g, d	C_2H_5OH + $AgNO_3$			C_3H_7OH + $AgNO_3$	3060 ± 30	1400
a	CH_3OH + AgF	3620 ± 30	1760	C_4H_9OH + AgF	3660 ± 30	1640

—ment in the term ^2P and the splitting of this term into two or three levels, depending on the symmetry of the field of the matrix (2). The ground state $^2S_{1/2}$ is not split by electric fields. The inequality of the line widths in a doublet may arise as a result of partial splitting of that level of the doublet which is doubly degenerate. Such partial splitting may appear if, in the electric field of the matrix, there is a weak component of low symmetry.

The presence in one spectrum of several doublets and triplets is probably connected with the stabilization of silver atoms in several different types of trapping sites in one and the same matrix. The existence of such different types of trapping sites for silver atoms in frozen solutions was established in Ref. (1).

Additional shifts and broadenings of lines in the absorption spectra of stabilized atoms may arise because of differences in the interaction potentials with the surrounding particles of the matrix for the ground and excited states of these atoms ($^{3-5}$).

For quantitative application to the optical absorption spectra of stabilized silver atoms of the theoretical considerations indicated above, detailed information is needed on the structure of the matrix in the region of the trapping sites of the atoms. We expect to obtain such information with the aid of paramagnetic resonance of these atoms (^{1}).

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CITED LITERATURE

1. R. A. Zhitnikov, A. L. Orbelí, *Fiz. tverd. tela*, **7**, No. 7 (1965).
2. H. A. Bethe, *Ann. Phys.*, **3**, 133 (1929).
3. M. MacCarty, G. W. Robinson, *Mol. Phys.*, **2**, 415 (1959).
4. W. Weyhmann, F. M. Pipkin, *Phys. Rev.*, **137**, A490 (1965).
5. O. Schnepp, *J. Phys. Chem. Sol.*, **17**, 188 (1961).

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